

## CO HYDROGENATION ON ZEOLITE-SUPPORTED Ru: EFFECT OF NEUTRALIZING CATIONS

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### INTRODUCTION

Previous results for zeolite-supported Ru prepared by ion exchange suggested a possible effect of the nature and concentration of the neutralizing cations in the zeolite on the catalytic properties of the metal (1). However, the interpretation of these results was complicated by the fact that a series of zeolites with different Si/Al ratios was used.

The present study was undertaken to investigate systematically the influence of the nature of alkali neutralizing cations on CO hydrogenation over ion-exchanged Y-zeolite-supported ruthenium catalysts.

### EXPERIMENTAL

A series of RuY catalysts was prepared from  $\text{NH}_4\text{Y}$ ,  $\text{LiY}$ ,  $\text{NaY}$ ,  $\text{KY}$ ,  $\text{RbY}$ , and  $\text{CsY}$  zeolites by ion-exchange with  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ . After decomposition under vacuum and reduction in hydrogen at 673 K, the resulting Ru catalysts were characterized by atomic absorption and chemisorption of hydrogen and carbon monoxide.

CO hydrogenation was carried out in a tubular microreactor where the prereduced catalyst (0.25 g) was first rereduced in a hydrogen stream at 673 K for two hours before cooling to reaction temperature. The reaction was carried out at atmospheric pressure and 483-573 K using 1:1 mixture of  $\text{H}_2$  and CO. A sample of the effluent gas was analyzed on-line by gas chromatography after five minutes of reaction. The hydrogen bracketing technique was used to maintain a clean metallic surface.

### RESULTS AND DISCUSSION

#### Catalytic Activity and Product Distribution

Hydrogen chemisorption measurements were used to calculate the Ru dispersion (Table I) as described in (2). Based on both  $\text{H}_2$  and CO chemisorption results it was concluded that the metal dispersions were high and similar in the various Y-zeolites, except for RuHY.

Table I compares the turnover frequencies (TOF) at 523 K for CO conversion on the various catalysts, as well as the product distributions. No significant effect of the nature of the neutralizing alkali cations on TOF nor on the selectivity for  $\text{CH}_4$  and the chain growth probability were observed. Having similar metal loadings, the concentrations of the structural hydroxyl groups, formed during the reduction of the ruthenium ions in  $\text{LiY}$ ,  $\text{NaY}$ ,  $\text{KY}$ ,  $\text{RbY}$ , and  $\text{CsY}$ , should be comparable in all these catalysts.

TABLE I

CATALYTIC PROPERTIES OF ZEOLITE-SUPPORTED RU CATALYSTS AT 523 K

Catal.	Load. (wt%)	Disp. (%)	TOF (s <sup>-1</sup> × 10 <sup>3</sup> )	Selectivity (wt%)					
				C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
RuHY	3.8	30	40.5	34.3	13.7	19.1	17.1	12.3	3.5
RuLiY	3.4	53	10.7	33.4	14.3	21.8	17.6	11.8	1.1
RuNaY	3.8	67	6.9	32.7	14.0	21.5	17.0	10.9	3.9
RuKY	3.2	52	8.0	30.7	13.7	23.5	15.8	11.0	5.2
RuRbY	3.6	49	14.1	33.5	14.4	22.0	15.3	9.7	5.1
RuCsY	3.7	56	12.4	36.1	13.2	21.6	15.1	9.8	4.2

It is generally accepted that for alkali cation zeolites, exchange of sodium ions for smaller or larger cations produces a change in the electrostatic field inside the zeolites, and hence a change in the strength of their acid sites (3-4). However one possible reason why these different acid sites have no significant effect on the catalytic properties of the metal is the "neutralization" of these sites by olefins adsorbed on them (5), thus interrupting any possible interactions that these acid sites might have with the metal particles. Such interactions have been often suggested to be responsible for the observed changes in adsorption properties of zeolite-supported metals (6-7). The higher activity observed for RuHY is probably due in large part to the fact that the Ru particles were significantly larger in this catalyst.

The apparent activation energy for CO conversion,  $E_a$ , varied with the neutralizing cation employed. A plot of  $E_a$  versus the crystal ionic radius of the initial charge balancing cations suggests that Ru is more uniformly distributed throughout the zeolite crystallites for the small cation zeolites. In the larger cation zeolites, Ru is probably preferentially distributed in the external shell of the zeolite crystallites. Although this uniform versus shell distribution, if true, does not seem to affect the % dispersion of the reduced Ru, but it affects the activation energy of reaction by introducing diffusion limitations on reactants and products for the zeolite catalysts having smaller neutralizing cations. This is further confirmed by the non-linearity of the Arrhenius plots for these catalysts.

#### Secondary Olefin Transformations

The nature of the neutralizing cations in Y-zeolites was found to have a strong influence on the olefin-to-paraffin ratios ( $C_3^-/C_3^-$ ), regardless of whether the comparison was made at constant temperature (Figure 2) or constant CO conversion. The  $C_3^-/C_3^-$  ratio was highest where the larger alkali cations had been exchanged into the zeolite and followed the sequence: Cs ~

Rb > K > Na > Li ~ H. The variation in the amount of isobutane in the C<sub>4</sub>-fraction is also included in Figure 2 as this reflects the secondary acid-catalyzed reactions which were enhanced in the order: Cs ~ Rb < K << Na < Li << H. The results listed in Table II show that at 523 K RuHY gave 53% isobutane (based on the total amount of C<sub>4</sub>). When this catalyst was exchanged after reduction with a dilute solution of K<sub>2</sub>CO<sub>3</sub>, in order to replace H<sup>+</sup> by K<sup>+</sup>, the isobutane was no longer obtained and the propene-to-propane ratio increased to 16.9. On the other hand, RuRbY yielded only very small quantities of isobutane, but, when 0.2 g of HY was added at the tail end of the reactor bed in a separate layer, the isobutane content of the C<sub>4</sub>-fraction increased to 30%, and the C<sub>3</sub><sup>-</sup>/C<sub>3</sub> ratio dropped from 6.4 to 4.1.

These results provide strong evidence that the hydrocarbon products of CO hydrogenation over supported ruthenium catalysts are mainly, if not totally, desorbed as olefins which can then undergo secondary reactions on the acid sites or to a lesser extent hydrogenation on the metal sites.

TABLE II

EFFECT OF ACIDITY ON OLEFIN AND ISOBUTANE SELECTIVITIES

Catalyst	Propene/Propene Ratio	Isobutane (wt% in C <sub>4</sub> )
RuHY	1.1	53.0
RuHY(K) (a)	16.9	0.0
RuRbY	6.4	1.4
RuRbY+HY (b)	4.1	30.6

(a) RuHY treated in 0.1 N K<sub>2</sub>CO<sub>3</sub> solution after reduction.

(b) RuRbY and HY in separate layers.

The most important acid-catalyzed reactions of olefins are isomerization, oligomerization, disproportionation, hydrogenation by hydride transfer, and coke formation. The rate of these reactions are influenced by the concentration and the acid strength of the hydroxyl groups present in the zeolite (8). The decrease of the olefin-to-paraffin ratio with decreasing cation radius, paralleled by an increasing acidity strength, may be partly explained by the enhancement of hydrogen transfer reactions catalyzed by acid sites. Several studies (8-10) of acid-catalyzed olefin reactions have demonstrated that the interaction of acidic hydroxyl groups with adsorbed olefins is accompanied by olefin oligomerization. At temperatures higher than 370 K, the olefin oligomers decompose by a disproportionation mechanism to produce gaseous paraffins and some polyene species which remain on the zeolite (8). The primary olefinic products may be hydrogenated on the acid sites, not only by hydrogen resulting from the oligomer decomposition, but also by hydrogen supplied by spillover from the metal to the support. However, the effect of mass transfer

limitations on the propene-to-propane ratio due to a uniform versus shell distribution of Ru in the zeolite cannot be ruled out. The increase in residence time of olefins following their formation may result in an increased probability for readsorption on the metal sites and hydrogenation.

It has also been shown that the higher the concentration and strength of the acid sites in a zeolite, the more branched the olefin oligomers (8). Thus, decomposition of the oligomers formed on the more acidic zeolites would result in the formation of more isoparaffins. The trend in selectivity for isobutane suggests that the nature of the alkali cations modify the strength of the acid sites. A possible effect of diffusion and steric factors may also account for this trend in selectivity for isobutane.

#### CONCLUSION

The nature of the charge balancing cations in zeolites can have a marked effect on the catalytic properties of ruthenium for CO hydrogenation in ion-exchanged zeolite-supported Ru catalysts. Although it has hardly any influence on the specific activity of the catalysts or on the overall chain growth probability, the nature of the neutralizing cations has a pronounced effect on the selectivities for olefins and branched hydrocarbons. Variations in the strength of the acid sites with the nature of these cations as well as mass transfer limitations apparently play a major role in shaping the olefin and isoparaffin selectivities.

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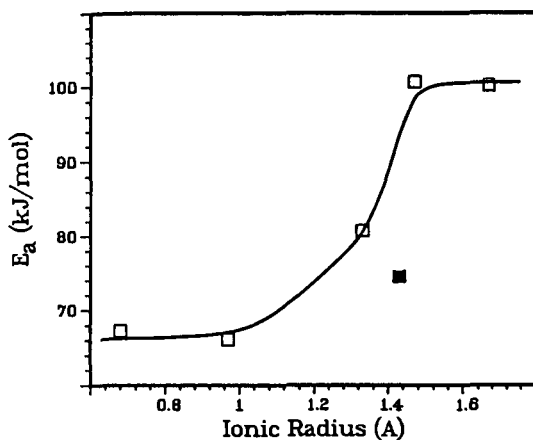


Figure 1. Variation in  $E_a$  with neutralizing cation radius; (■) RuHY.

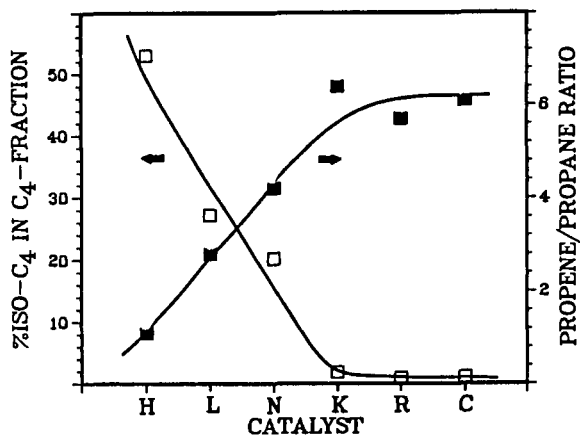


Figure 2. Effect of neutralizing cation on olefin fraction and isobutane formation; Catalysts: (H) RuHY, (L) RuLiY, (N) RuNaY, (K) RuKY, (R) RuRbY, (C) RuCsY.